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Mass transfer across fluid interfaces - modeling the influence of adsorbed surfactant

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Abstract

This note reports on an extended sharp-interface model for two-phase flows with mass transfer which accounts for the effect of interface contamination with surface active agents (surfactants). Besides the influence on mass transfer mediated by the back-effect of the adsorbed surfactant onto the hydrodynamics via changes in interfacial tension, this model also describes the local hindrance of mass transfer due to interface coverage in a thermodynamically consistent way. Depending on the interfacial free energy, the latter is closely related to Langmuir's energy barrier model.

Keywords: Mass transfer hindrance, soluble surfactant, interface chemical potentials, interfacial entropy production, jump conditions.

In continuum mechanical descriptions of mass transfer across fluid interfaces one common approach employs the sharp-interface assumption, i.e. the interface between the contacting bulk phases is a surface of zero thickness. Assuming constant density or small Mach number flows, the standard sharp-interface model is then based on the incompressible two-phase Navier-Stokes equations for fluid systems without phase change. Inside the fluid phases the governing equations are

$$\nabla \cdot \mathbf{v} = 0, \tag{1}$$

$$\partial_t(\rho\mathbf{v}) + \nabla \cdot (\rho\mathbf{v} \otimes \mathbf{v}) + \nabla p = \nabla \cdot \mathbf{S}^{\mathrm{visc}} + \rho\mathbf{g} \tag{2}$$

with the viscous stress tensor

$$\mathbf{S}^{\mathrm{visc}} = \eta(\nabla\mathbf{v} + \nabla\mathbf{v}^{\mathsf{T}}), \tag{3}$$

where the material parameters depend on the respective phase. The standard interfacial jump conditions for total mass and momentum are

$$[\![\mathbf{v}]\!] = 0, \quad [\![-\mathbf{S}]\!] \cdot \mathbf{n}_\Sigma = \sigma\kappa_\Sigma\mathbf{n}_\Sigma + \nabla_\Sigma\sigma, \tag{4}$$

where $\mathbf{S} = -p\mathbf{I} + \mathbf{S}^{\mathrm{visc}}$ is the stress tensor, $\kappa_\Sigma = -\nabla \cdot \mathbf{n}_\Sigma$ is twice the mean curvature of the interface and ∇_Σ denotes the surface gradient. Here $\mathbf{n}_\Sigma$ is the unit normal at the interface directed into one of the bulk phases and

$$[\![\phi]\!](\mathbf{x}) = \lim_{h\to 0+} \big(\phi(\mathbf{x} + h\mathbf{n}_\Sigma) - \phi(\mathbf{x} - h\mathbf{n}_\Sigma)\big) \tag{5}$$

denotes the jump of a field ϕ across the interface.

The local molar concentration c_i of a chemical species A_i is governed by the balance equation

$$\partial_t c_i + \nabla \cdot (c_i \mathbf{v} + \mathbf{J}_i) = r_i, \tag{6}$$

where the molecular fluxes $\mathbf{J}_i$ are typically modeled according to Fick's law as

$$\mathbf{J}_i = -D_i \nabla c_i \tag{7}$$

with constant diffusivity. The source term on the right-hand side in (6) accounts for chemical reactions. At the interface, the diffusive fluxes in normal direction are usually supposed to be continuous, i.e.

$$[\![\mathbf{J}_i]\!] \cdot \mathbf{n}_\Sigma = 0. \tag{8}$$

Another jump condition is needed to determine the concentration profiles of A_i, which is not a balance but a constitutive relation. The standard relation is to assume continuity of the chemical potentials at the interface, i.e.

$$[\![\mu_i]\!] = 0. \tag{9}$$

Employing specific assumptions on the μ_i, for instance dilute transfer component A_i, this leads to Henry's law, i.e.

$$c_k^- = c_k^+ / H_k; \tag{10}$$

here the Henry coefficient H_k is usually assumed to be constant. Throughout this paper, the superscripts $\pm$ are used to distinguish between the two bulk phases. Equations (1)–(4) and (6)–(10) comprise what we call the "standard model". This standard model, sometimes with further simplifications like constant surface tension, homogeneous gas phase concentrations or even constant liquid-sided concentration at the interface, is the basis of almost all detailed numerical simulations of mass transfer across fluid interfaces up to now; see [4] and the extensive list of references given there.

If a constituent A_i of the fluid mixture is surface active, it adsorbs on the interface and, typically, lowers the surface tension. For such a surfactant, a non zero area-specific concentration has to be accounted for. Hence the mass balance for A_i on the interface becomes more involved and reads

$$\partial_t^\Sigma c_i^\Sigma + \nabla_\Sigma \cdot (c_i^\Sigma \mathbf{v}^\Sigma + \mathbf{J}_i^\Sigma) + [\![c_i(\mathbf{v} - \mathbf{v}^\Sigma) + \mathbf{J}_i]\!] \cdot \mathbf{n}_\Sigma = \mathbf{r}_i^\Sigma, \tag{11}$$

where $\mathbf{v}^\Sigma$ denotes the interface barycentric velocity, $\mathbf{J}_i^\Sigma$ the interfacial diffusive flux and r_i^Σ is the total molar rate of change of A_i due to interface chemical reactions between the species. Furthermore, ∂_t^Σ denotes the time derivative taken along a path which follows the interface's normal motion; this is sometimes called Thomas derivative. Note that even for vanishing interface concentrations and without interface chemistry, equation (11) does not reduce to (8), but the resulting jump condition contains a term related to the relative motion of the interface to the bulk matter. This is crucial, for example, to model the condensation of a vapor bubble or the dissolution of a pure gas bubble.

While the interface contributions in the partial *mass* balances are of crucial importance, their *inertia* can often be neglected. Assuming, in addition, that no

intrinsic interface viscosities appear, the interfacial momentum balance becomes a momentum transmission condition which reads as

$$[\![\dot{m}\mathbf{v}]\!] = [\![\mathbf{S}]\!] \cdot \mathbf{n}_\Sigma + \sigma\kappa_\Sigma \mathbf{n}_\Sigma + \nabla_\Sigma \sigma \tag{12}$$

and generalizes (4). If surfactant is present, the surface tension depends (strongly) on the interfacial concentrations. This is described by a surface equation of state, i.e. $\sigma = \sigma(c_1^\Sigma, \ldots, c_N^\Sigma)$ in the isothermal case – in general, σ also depends on temperature. Then the last term in (12), which represents the so-called Marangoni stress, becomes

$$\nabla_\Sigma \sigma = \sum_{i=1}^{N} \frac{\partial \sigma}{\partial c_i^\Sigma} \nabla_\Sigma c_i^\Sigma. \tag{13}$$

Now note that for stagnant fluids, (12) reduces to

$$[\![p]\!]\mathbf{n}_\Sigma = \sigma\kappa_\Sigma \mathbf{n}_\Sigma + \nabla_\Sigma \sigma. \tag{14}$$

The normal component of (14) implies the Young-Laplace law, i.e.

$$p^+ - p^- = \frac{2\sigma}{R} \tag{15}$$

in case of spherical bubbles or droplets of radius R, while the tangential part implies constant surface tension (individually on connected interface components), since there is no term to balance the tangentially acting Marangoni stress. The important consequence of this is that a non-zero Marangoni stress induces a flow at the interface, the so-called Marangoni convection, which usually has a significant impact on mass transfer processes.

Up to here, mass transfer hindrance due to surface coverage is not yet included in the model. For this to be done, the crucial step is to include for *every transfer component*, i.e. any A_i with non-zero concentrations on both sides of the interface, a possibly non-zero interfacial concentration. For better understanding of this point note that in the sharp-interface model, the interface in fact represents a thin layer in which the partial mass densities change from one to the other (local) bulk value along a distance δ in the order of a few Ångström. Since every transfer component A_i of the mixture, in principle every constituent, is also present in this layer, it has a non-zero interface concentration c_i^Σ, hence its modeling requires the extended mass balance as used for soluble surfactant. For every constituent we therefore include the corresponding partial mass balance

$$\partial_t^\Sigma \rho_i^\Sigma + \nabla_\Sigma \cdot (\rho_i^\Sigma \mathbf{v}^\Sigma + \mathbf{j}_i^\Sigma) + [\![\rho_i(\mathbf{v} - \mathbf{v}^\Sigma) + \mathbf{j}_i]\!] \cdot \mathbf{n}_\Sigma = M_i r_i^\Sigma, \tag{16}$$

where $\rho_i^\Sigma = M_i c_i^\Sigma$ and $\mathbf{j}_i^\Sigma = M_i \mathbf{J}_i^\Sigma$ with M_i denoting the molar mass. It is now helpful to write out the jump-bracket, i.e.

$$[\![\rho_i(\mathbf{v}-\mathbf{v}^\Sigma)+\mathbf{j}_i]\!]\cdot\mathbf{n}_\Sigma = -(\rho_i^+(\mathbf{v}^+-\mathbf{v}^\Sigma)+\mathbf{j}_i^+)\cdot\mathbf{n}^+ - (\rho_i^-(\mathbf{v}^--\mathbf{v}^\Sigma)+\mathbf{j}_i^-)\cdot\mathbf{n}^- \tag{17}$$

with $\mathbf{n}^\pm$ denoting the outer unit normals to the respective bulk phases. We abbreviate the terms on the right-hand side by letting

$$\dot{m}_i^{\pm,\Sigma} = (\rho_i^\pm(\mathbf{v}^\pm - \mathbf{v}^\Sigma) + \mathbf{j}_i^\pm) \cdot \mathbf{n}^\pm, \tag{18}$$

and further split the one-sided mass transfer terms into an adsorption and a desorption term according to

$$\dot{m}_i^{+,\Sigma} = s_i^{ad,+} - s_i^{de,+}, \quad \dot{m}_i^{-,\Sigma} = s_i^{ad,-} - s_i^{de,-}. \tag{19}$$

The crucial point is that now, i.e. in case that the interface can carry also a transfer component A_i, the transfer of A_i from bulk phase + to bulk phase −, say, is modeled as the sequence of a sorption process from phase + onto the interface followed by another sorption process from Σ to bulk phase −. The one-sided sorption rates need to be modeled using constitutive, i.e. material-dependent, relations. We skip the details and refer to [2] and the references given there, while for fundamentals on continuum mechanical modeling of two-phase fluid systems in general we refer in particular to [7, 6, 1, 9]. Let us only report that, if kinetic and viscous terms in the entropy production due to mass transfer are ignored, and if a nonlinear closure as for chemical reactions is applied, the resulting closure relations read as

$$\ln \frac{s_i^{ad,\pm}}{s_i^{de,\pm}} = \frac{a_i^{\pm}}{RT}\big(\mu_i^{\pm} - \mu_i^{\Sigma}\big) \quad \text{with} \quad a_i^{\pm} \geq 0. \tag{20}$$

Now one of the rates, either the ad- or the desorption rate, has to be modeled based on a micro-theory or experimental knowledge, while the other rate then follows from (20). Skipping again the detailed derivation which can be found in [2], we only report the resulting relation if desorption is modeled as $s_i^{de} = k_i^{de} x_i^{\Sigma}$ with $x_i^{\Sigma} = c_i^{\Sigma}/c^{\Sigma}$ denoting the interfacial molar fraction and under the assumption of ideal mixtures both in the bulk phase and on the interface. Employing $a_i^{\pm} = 1$ in (20) and assuming

$$[\![\dot{m}_i]\!] = 0 \quad \Leftrightarrow \quad \dot{m}_i^{+,\Sigma} + \dot{m}_i^{-,\Sigma} = 0 \tag{21}$$

which corresponds to negligible accumulation of the transfer component on the interface (while still accounting for the interfacial concentration in the thermodynamics), one obtains the closure relation for the mass transfer rate of A_i as

$$\dot{m}_i^{+,\Sigma} (= -\dot{m}_i^{-,\Sigma}) = k_i \exp\big(-\frac{g_i^{\Sigma}}{RT}\big)\left(\exp\big(\frac{g_i^{+}}{RT}\big)x_i^{+} - \exp\big(\frac{g_i^{-}}{RT}\big)x_i^{-}\right) \tag{22}$$

with a transfer rate constant k_i which depends on the sorption rate constants. In (22), the quantity g_i is the Gibbs free energy of the pure substance A_i but under the temperature and pressure as locally present in the respective bulk phase or on the interface. For comparison, let us report that the analogous modeling but without interface concentrations yields

$$\dot{m}_i^{+,\Sigma} (= -\dot{m}_i^{-,\Sigma}) = k_i \exp\big(-\frac{g_i^{-}}{RT}\big)\left(\exp\big(\frac{g_i^{+}}{RT}\big)x_i^{+} - \exp\big(\frac{g_i^{-}}{RT}\big)x_i^{-}\right). \tag{23}$$

The most important difference is that in (22) the mass transfer rate is influenced by the surface tension via the surface Gibbs free energy, which accounts for the effect of surfactants on the mass transfer of the considered transfer component.

Concrete forms of the mass transfer relation (22) of course depend on the employed model for the free energies. For example, assume the surface equation

of state to be given as

$$p^\Sigma = RT \sum_{i=1}^{N-1} c_i^\Sigma + K^\Sigma \Big(\frac{c_N^\Sigma}{c_{\text{ref}}^\Sigma} - 1 \Big). \tag{24}$$

The idea behind (24) is that the interface with its surface tension in the clean state is built by component A_N (the solvent, say) as the phase boundary between a liquid and a vapor phase. The phase boundary is modeled as a compressible interface phase with compressibility K^Σ. Then a consistent interface free energy is given by

$$\rho^\Sigma \psi^\Sigma = -p^\Sigma + (K^\Sigma + p^\Sigma) \ln\big(1 + \frac{p^\Sigma}{K^\Sigma}\big) + RT \sum_{i=1}^{N} c_i^\Sigma \ln x_i^\Sigma. \tag{25}$$

Under these assumptions, (22) yields

$$\dot{m}_i^{+,\Sigma} = \frac{k_i}{1 + p^\Sigma / K^\Sigma} \left(\exp\big(\frac{g_i^+}{RT}\big) x_i^+ - \exp\big(\frac{g_i^-}{RT}\big) x_i^- \right). \tag{26}$$

Taking the clean surface as the reference state, this yields

$$\dot{m}_i^{\text{contam}} = \frac{1 + p_{\text{clean}}^\Sigma / K^\Sigma}{1 + p_{\text{contam}}^\Sigma / K^\Sigma} \, \dot{m}_i^{\text{clean}} = \frac{K^\Sigma - \sigma_{\text{clean}}}{K^\Sigma - \sigma_{\text{contam}}} \, \dot{m}_i^{\text{clean}} \tag{27}$$

for the mass transfer in a system contaminated by surfactant, given as a multiple of that in the clean system. The specific relation (27) evidently results from strong assumptions which are not realistic in particular for high surfactant concentrations. To account for the (different) area demands of the adsorbed species, a possible surface equation of state is

$$p^\Sigma = -K^\Sigma + \frac{RT}{1 - \theta} \sum_{i=1}^{N} \alpha_i c_i^\Sigma \quad \text{with} \quad \theta = \sum_{i=1}^{N} c_i^\Sigma / c_i^{\Sigma,\infty}, \tag{28}$$

where θ is the total coverage of the interface. Then the surface analog of the construction of a consistent free energy as explained in §15 in [3] yields the corresponding interface free energy as

$$\rho^\Sigma \psi^\Sigma = -(1 - \theta) p^\Sigma + RT \sum_{i=1}^{N} \alpha_i c_i^\Sigma \ln\big(1 + \frac{p^\Sigma}{K^\Sigma}\big) + RT \sum_{i=1}^{N} c_i^\Sigma \ln x_i^\Sigma. \tag{29}$$

The corresponding (molar based) chemical potentials then are

$$\mu_i^\Sigma = g_i^\Sigma(T, p^\Sigma) + RT \ln x_i^\Sigma \quad \text{for } i = 1, \ldots, N-1 \tag{30}$$

with

$$g_i^\Sigma(T, p^\Sigma) = \frac{p^\Sigma}{c_i^{\Sigma,\infty}} + RT\alpha_i \ln\big(1 + \frac{p^\Sigma}{K^\Sigma}\big) \quad \text{for } i = 1, \ldots, N-1. \tag{31}$$

Insertion of (31) into (22) implies the relation

$$\dot{m}_i^{+,\Sigma} = \frac{k_i}{(1 + p^\Sigma / K^\Sigma)^{\alpha_i}} \exp\big(\frac{-p^\Sigma}{c_i^{\Sigma,\infty} RT}\big) \left(\exp\big(\frac{g_i^+}{RT}\big) x_i^+ - \exp\big(\frac{g_i^-}{RT}\big) x_i^- \right). \tag{32}$$

Taking again the clean surface as the reference state, this yields

$$\dot{m}_i^{\text{contam}} = \Big(\frac{K^\Sigma - \sigma_{\text{clean}}}{K^\Sigma - \sigma_{\text{contam}}}\Big)^{\alpha_i} \exp\Big(-\frac{\sigma_{\text{clean}} - \sigma_{\text{contam}}}{c_i^{\Sigma,\infty} RT}\Big)\dot{m}_i^{\text{clean}}. \tag{33}$$

The additional mass transfer reduction in (33) as compared to (27) corresponds to an exponential damping factor of Boltzmann type, i.e. a factor of the form $k\exp(-a\,p^\Sigma/RT)$, in accordance with the energy barrier model due to Langmuir; see [8], [5] and the references given there.

Experimental data for the transfer of CO_2 from Taylor bubbles under the influence of different surfactants in [10] supports the fact that the surface pressure of the contaminated system - not, in the first place, the surfactant concentration - determines the mass transfer reduction.

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